PLASTICS LABORATORY
TECHNICAL REPORT

No. 66D

ELECTRONIC PROPERTIES AND STRUCTURE IN
CONJUGATED POLYMERIC SYSTEMS

R. P. Chartoff and C. Cappas

February 15, 1963

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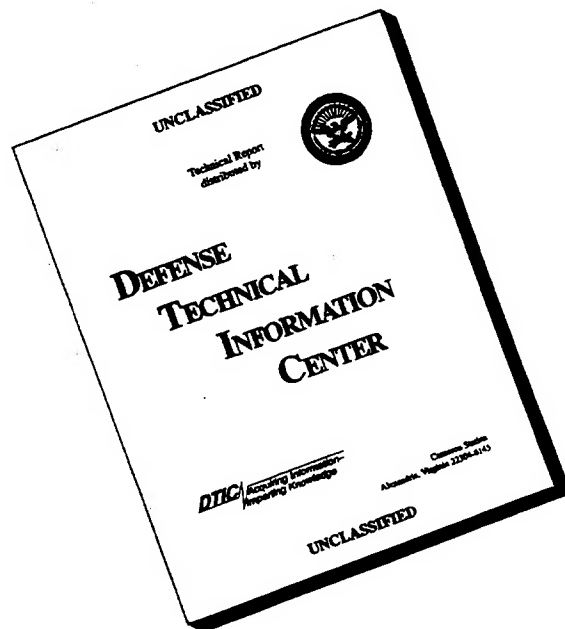# PRINCETON UNIVERSITY
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ABSTRACT

The relation between chemical structure and electronic properties for three classes of organic polymers with systems of conjugated double bonds was studied. The three classes include linear polyalkynes, wholly aromatic polybenzimidazoles, and highly crosslinked polyacene quinone radical (PAQR) polymers,

The wide range of electronic properties observed for these polymers lends support to the view that highly conjugated polymer molecules exist in the form of stable biradicals and that the enhanced electronic behavior of these materials is directly related to the biradical population which may be observed by electron spin resonance spectroscopy.

Infrared absorption spectra were obtained for several PAQR polymers by the KBr pressed disk technique, and a structure consistent with spectroscopic and chemical evidence has been proposed for phenolphthalein PAQR polymers.

16 figs. 32 refs.

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# INTRODUCTION

The synthesis and study of the properties of semiconducting polymers is a new and promising aspect of the chemistry of macromolecular materials (1,2,3,4).

In general, polymers exhibiting enhanced electrical conductivity have conjugated double bonds in their chain backbones. Conjugated polymers of this type have variously been subdivided into groups of those having acyclic (linear) systems of conjugated bonds, and those containing aromatic, heterocyclic, and metallocyclic structures in their main chains (1,2).

The orbitals of the $\pi$-electrons in a conjugated molecule can be considered as overlapping with the resulting coalescence of wave functions forming a single $\pi$-orbital which encompasses all the nuclei of the conjugated system (5,6). Because of this resonance, the $\pi$-electrons are delocalized. Thus an electrical disturbance at one part of the molecule should theoretically be transmitted throughout the system.

It is well known (5,6,7) that delocalization causes a decrease in the internal energy of the system resulting in a molecule which has greater thermodynamic stability. Many highly conjugated polymers have been found to possess thermal stability at temperatures in excess of 400°C (1,8, 10).

Delocalization of the π-electrons in conjugated polymer molecules also results in a decrease in the excitation energy necessary to promote π-electrons to the triplet state because of the decrease in the energy difference between the highest filled electronic level and the lowest unfilled level. The decrease in the energy necessary for excitation to the triplet state and the accompanying decrease in the ionization potential in highly conjugated systems are, no doubt, largely responsible for the observed semiconductivity, magnetic, optical, and chemical properties of these materials (1).

Recent interest in the unusual properties of these highly conjugated polymers has prompted the development of several new classes of synthetic materials which exhibit enhanced electrical properties. Soviet scientists are among the leaders in synthesizing and characterizing various highly conjugated polymers including representatives of each of the groups mentioned above. Their work in this area has been reviewed by Berlin (1) and Semenov (9).

Typical of the polymers studied by Soviet workers are: polyalkynes including polyacetylene, polyphenylacetylene, polybutyne-1, and polyhexyne-1; polyazophenylenes (10); polyphenylene quinones and their chelates· and polymeric chelates prepared by the reaction of tetracyanoethylene with metals.

Many other workers have also become interested in the synthesis and properties of semiconducting polymers. Hatano, Kambara, and Okamoto (11) have reported their preliminary findings in a study involving the synthesis and characterization of a series of polyacetylenes. Watson, McGordie, and Lands (12) studied the polymerization of acetylene, propyne, and butyne-1, and are now investigating the electrical and magnetic properties of the polymers they produced.

Pohl (3,4) and coworkers have studied the properties of many polyacene quinone radical (PAQR) polymers produced by the condensation of aromatic hydrocarbons or their derivatives with aromatic acid anhydrides. McNeill and Weiss (13) synthesized polyxanthenes from hydroquinone, phthalic anhydride, and pyromellitic anhydride. Epstein and Wildi (14) studied the electrical properties of poly-copper phthalocyanine synthesized from a mixture of pyromellitonitrile, cuprous chloride, and urea. Vogel and Marvel (8) synthesized polybenzimidazoles from aromatic tetramines and bifunctional aromatic acids. These polymers have completely conjugated aromatic structures, but their electrical properties have not been studied.

As experimental data on semiconducting polymers have accumulated, it has become quite apparent that the

manifestation of various properties in polymers with conjugated double bonds depends on several parameters including: (a) the length and structure of the basic conjugated chain: (b) the nature and degree of conjugation of side groups: (c) the presence of heteroatoms in the chain; and (d) the physical state of the polymer (1,2).

A considerable amount of uncertainty and confusion in this area persists, however, due to the relative dearth of data available as yet on polymeric materials of this type.

The purpose of this investigation was to add to and help clarify the growing body of knowledge on the characteristics of molecular structure which contribute to enhanced electrical and magnetic properties in high polymers.

## MATERIALS

The following classes of polymers with conjugated double bonds were chosen for this study:

1. polyalkynes
2. polybenzimidazoles
3. polyacene quinone radical (PAQR) polymers

These three classes cover a range from the most simple of the highly conjugated polymers, the linear polyalkynes, to one of the most complex, the crosslinked PAQR polymers.

Polyalkynes:

Various alkyl and arylacetylenes may be polymerized at room temperature or somewhat elevated temperature (30-70°C) in the presence of a Ziegler-type catalyst (composed of a transition metal halide and a metal alkyl) (1,11,12).

Samples of polypropyne, polybutyne-1, polypentyne-1, and polyphenylacetylene of the highest possible purity were prepared by the Polymer Corporation Limited of Sarnia, Canada and sent to this Laboratory in glass containers sealed under nitrogen. The samples had been dried for three days at a pressure of $10^{-1}$ mm Hg before being sealed.

Polypentyne-1 and polybutyne-1 were deep black
in color, soft and rubbery. The polyphenylacetylene sam-
ple was deep orange in color and powdery. Polypropyne
appeared to be a crusty granular material, orange in color.

X-ray spectra showed that the polymers were not
crystalline but did possess a preferred periodicity. In-
frared and ultraviolet spectra indicated that a high de-
gree of conjugated unsaturation was present but some de-
gree of unconjugated unsaturation was also present. In-
trinsic viscosity and solubility data for these polymers
are cited in Table I (32).

Polybenzimidazoles:

Polybenzimidazoles (8) may be prepared by the
melt polycondensation of aromatic tetramines and the di-
phenyl esters of aromatic dicarboxylic acids. They are
completely conjugated, wholly aromatic polymers contain-
ing heteroatoms in their conjugated chains and are char-
acterized by a high degree of stability. They are highly
resistant to treatment with hydrolytic media and can with-
stand continued exposure at elevated temperatures. The
polymers are soluble in concentrated sulfuric acid and
formic acid, producing stable solutions. Most of them
are also soluble in dimethylsulfoxide.

Table I

Polyalkyne $[\eta]$ and
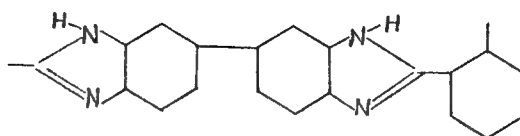solubility in toluene
at 30.1°C (32)

| Polymer | $[\eta]\ \dfrac{g^{-1}}{100\ cc}$ | solubility (%) |
|---|---|---|
| polypropyne | 0.07 | 100 |
| polybutyne-1 | 0.16 | 99 |
| polypentyne-1 | 0.21 | 93 |
| polyphenylacetylene | 0.16 | 96 |

# Table 2. Polybenzimidazole Structure

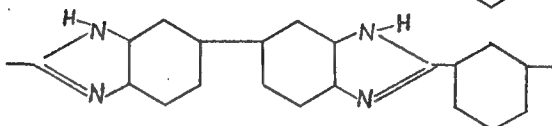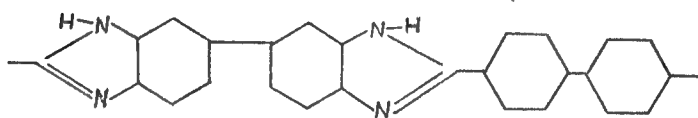Polymer Number          Repeating Unit
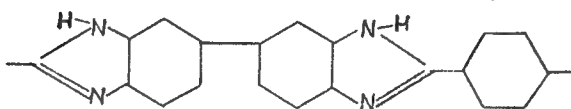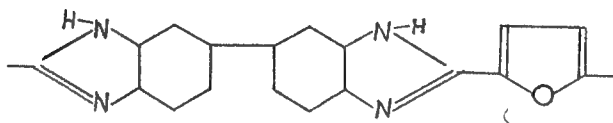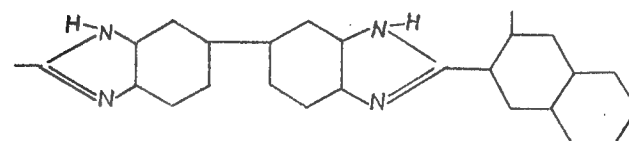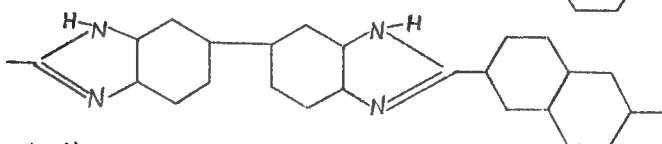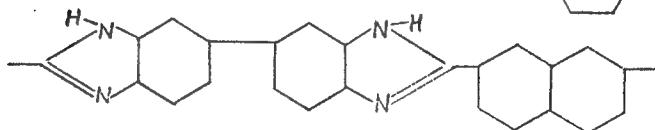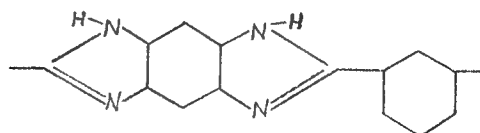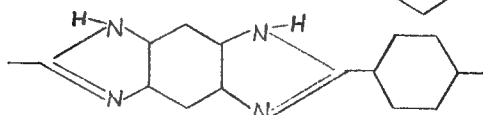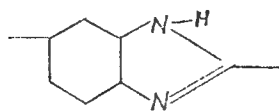
Samples of eleven well characterized (8) poly-
benzimidazoles were obtained for study from Professor
C. S. Marvel: their structures are shown in Table 2.

Polyacene quinone radical polymers:

PAQR polymers may be prepared by the melt poly-
condensation of an aromatic hydrocarbon or its derivative
with an aromatic acid or acid anhydride. The reaction is
usually carried out at temperatures of 256 or 306°C with
zinc chloride as catalyst. The products of polymerization
are leached and extracted with a variety of polar and non-
polar solvents to remove impurities. In general, the poly-
mers formed are hard, infusible, deeply colored, and ap-
parently highly crosslinked materials. Pohl and coworkers
(15,16) have described the preparation of these polymers
in great detail.

Fresh samples of the polymers previously pre-
pared by Bornmann and Pohl (16) were synthesized. Repre-
sentatives of these with room temperature resistivities
varying from about $10^4$ ohm-cm to $10^{11}$ ohm-cm were chosen
for a more thorough examination of their electrical and
magnetic properties as well as their infrared absorption
spectra. The polymers selected, their room temperature
resistivities, and the materials used for their synthesis
are listed in Table 3.

Table 3

PAQR polymers used in
this investigation

| Sample No. | Reactants | Mole ratio reactants (catalyst $ZnCl_2$) | Reaction Temp. (°C) | Specific resistivity at 25°C (ohm-cm) |
|---|---|---|---|---|
| 3A | Anthraquinone Pyromellitic Anhydride | 3:1:2 | 306 | $2.0 \times 10^4$ |
| 19 | Phenanthrene Benzoic Acid | 1:1:1 | 256 | $2.4 \times 10^5$ |
| 7A | α naphthol-Phthalein Phthalic Anhydride | 2:1:1 | 256 | $6.5 \times 10^6$ |
| 26 | Anthracene Phthalic Anhydride | 2:1:2 | 256 | $9.5 \times 10^7$ |
| 6A | Phenol Phthalic Anhydride | 4:3:2 | 256 | $1.1 \times 10^8$ |
| 21 | Terephthaloyl Chloride Naphthalene | 1:1:1 | 256 | $6.0 \times 10^{11}$ |
| 9A | Phenolphthalein | 1:1 | 256 | $4.7 \times 10^8$ |
| 22 | Anthracene Terephthaloyl Chloride | 1:1:1 | 256 | $1.3 \times 10^8$ |
| 5 | Phenolphthalein Phthalic Anhydride | 2:1:2 | 256 | $8.8 \times 10^7$ |
| 13 | Phenanthrene Acetic Anhydride | 2:1:1 | 256 | $4.1 \times 10^8$ |

## Experimental Proceedures

The polymers examined in this investigation were generally available in finely powdered form. Great care was taken to ensure that the samples were dry before electrical measurements were made on them.

Resistivity measurements:

The resistivity of polymer pellets compacted between platinized steel electrodes was measured using a direct current technique (15, 17) with a Keithley Model 610A electrometer. Samples were precompacted at 4700 kg/cm$^2$ prior to the measurements which were made at a pressure of 1800 kg/cm$^2$. This condition was chosen so that the data obtained could be compared with the findings of previous workers (15,17). Pressure is known to have a significant effect on the resistivity of certain polymers (18).

A shielded, insulated, and thermostated aluminum box was used for the measurements of the variation of resistivity with temperature. Temperatures were measured with a copper-constantan thermocouple placed in close proximity to the sample (15).

Thermoelectric power:

A quantity of the polymer to be tested was clamped between two pieces of platinum foil supported by

aluminum blocks, one of which was heated electrically (15,17);
the whole cell was enclosed in a shielded, grounded box.
The potential between the electrodes was measured with a
Keithley Model 150A microvolt-ammeter for temperature dif-
ferences of up to 31C°.

Electron Spin resonance:

The concentration of unpaired electrons in samples
of certain PAQR polymers was determined by the application
of electron spin resonance spectroscopy.  A quantitative
spin assay was obtained for each sample (15) from the area
under the absorption curve by comparison with that of met-
allic lithium (used as a secondary standard).  The lithium
line was compared with the signal from a carefully purified,
solid crystalline sample of diphenylpicrylhydrazil of known
weight (used as a primary standard).

Infrared absorption spectroscopy:

Infrared spectra were obtained for several of
the PAQR polymers by the potassium bromide disk technique
(19).  Pellets were made with a Perkin-Elmer die heated to
about 60°C during the evacuation period.  The time required
for grinding the samples that were pressed was found to be
an important variable in the production of high quality pel-
lets.  If too long a grinding time was used the pellets
chipped and flaked on removal from the die.  The optimum

time for grinding samples varied from a short time for pure KBr to some longer time for a given quantity of polymer mixed with KBr (usually 2 mg. polymer in 400 mg. KBr). This optimum time was found by trial.

Spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer except for one case (sample 9A) where a spectrum was recorded on a Perkin-Elmer Model 421 grating spectrophotometer. Both of these are dual beam instruments and were used with a KBr reference beam.

## Results

A. <u>Variations of Resistivity with Temperature and the</u>
<u>Thermal Energy Interval</u>

One of the most important properties of semi-conductive materials is the temperature dependence of the electrical resistivity. In figures 1-3 the resistivity is plotted against reciprocal temperature for the various polymers studied here.

The temperature coefficient of the electrical resistivity $\rho$ is negative in every case, and a linear relationship exists between log $\rho$ and 1/T for the temperature range investigated. Since it is well known that this behavior is typical of semiconducting materials (3,11,15,17,20), it is assumed that the slight deviations from linearity observed in some cases result from insufficient time allowed for the system to reach thermal equilibrium.

The resistivity of these materials having an activation energy E for conduction may be given by the relationship.

$$\rho = \rho_0 \exp \frac{E}{kT} \tag{1}$$

$$\text{or} \quad \rho = \rho_0 \exp \frac{\Delta E}{2kT} \tag{2}$$

The term $\Delta E$ in equation (2) is usually associated with the energy required to produce mobile charge carriers and has therefore been termed an energy interval (20). The energy interval is coneventionally used instead of the activiation energy E because it is more convenient in the discussion of the energy gap in the band theory model of inorganic semiconductors. Although the quantity $\Delta E$ may be used to describe the thermal activation behavior of polymeric semiconductors, adherence to the band theory is not implied (4,15).

Values of the thermal energy interval computed from equation (2) are listed in Tables 4 and 5 along with $\rho_o$ values for the polymers studied. Values of $\Delta E$ from as low as 0.4 eV for the PAQR polymers to as high as 2.9 eV for the polybenzimidazoles were found.

$\Delta E$ values for polybutyne-1 and polypentyne-1 were not obtained because of the viscoelastic character of the materials. When compressed, these materials flowed excessively and therefore could not be retained between electrodes. An approximate measurement of the resistivity was obtained for polypentyne-1 by cooling the polymer below its glass transition temperature.

The temperature coefficient of resistivity for polyphenylacetylene and polypropyne was obtained by cooling

## Table 4

### Summary of Observed Electronic

### Properties for PAQR Polymers and Polyalkynes

| Sample | Resistivity 25°C $(\rho_{25})$(ohm-cm) | E(eV) | $\rho_0$ (ohm-cm) |
|---|---|---|---|
| 3A | $2.0 \ 10^4$ | 0.382 | 8.90 |
| 19 | $2.4 \ 10^5$ | 0.444 | 30.1 |
| 7A | $6.5 \ 10^6$ | 0.544 | 105 |
| 26 | $9.5 \ 10^7$ | 0.698 | 70.8 |
| 6A | $1.1 \ 10^8$ | 0.638 | 276 |
| 21 | $6.0 \ 10^{11}$ | 0.956 | 251 |
| | | | |
| polypentyne-1 | $3 \ 10^9$(10-15°C) | - - | - - - |
| polypropyne | $1.5 \ 10^{11}$ | 0.646 | $3.20 \ 10^5$ |
| polyphenylacetylene | $4.8 \ 10^{10}$ | 0.432 | $7.94 \ 10^6$ |

Table 5

Summary of Observed Electronic
Properties for Polybenzimidazoles

| Sample | Resistivity 25°C ($\rho_{25}$) (ohm-cm) | $\Delta$ E(eV) | $\rho_o$ (ohm-cm) |
|---|---|---|---|
| 9 | $4.1 \times 10^{10}$ | 1.12 | 7.1 |
| 6 | $1.3 \times 10^{13}$ | 1.39 | $3.2 \ 10^{-1}$ |
| 10 | $5.7 \times 10^{13}$ | 1.56 | 1.3 |
| 3 | $1.8 \times 10^{12}$ | 1.57 | $2.0 \times 10^{-2}$ |
| 6 | $3.2 \times 10^{15}$ | 1.66 | 7.9 |
| 8 | $1.0 \times 10^{14}$ | 1.78 | $6.3 \times 10^{-3}$ |
| 7 | $7.5 \times 10^{14}$ | 1.91 | $4.0 \times 10^{-4}$ |
| 2 | $9.0 \times 10^{11}$ | 2.15 | $3.2 \times 10^{-6}$ |
| 5 | $1.4 \times 10^{13}$ | 2.15 | $2.0 \times 10^{-5}$ |
| 1 | $5.0 \times 10^{12}$ | 2.23 | $1.6 \times 10^{-6}$ |
| 12 | $1.0 \times 10^{16}$ | 2.90 | $4.0 \times 10^{-10}$ |

the materials below room temperature to avoid the possibility of oxidizing them.

The data obtained for the polyalkynes studied here compare favorably with the results for polyacetylenes reported by Hatano, Kambara, and Okamoto (11).

B.  Thermoelectric Power and Figure of Merit

Seebeck coefficients (Q) were evaluated for two of the PAQR polymers having resistivities less than $10^6$ ohm-cm (the maximum resistivity value being set by the limitations of the measuring apparatus), by use of the relationship

$$Q = \frac{\Delta V}{\Delta T} \quad (microvolts/C\circ)$$

with an appropriate correction for the effect of platinum electrodes (15).

Sample  3A was found to have a Seebeck coefficient of 99 $\mu V/C^\circ$; the Seebeck coefficient for sample 19 was 217 $\mu V/C^\circ$.  These values are similar to those obtained for polymers studied by other workers (15).  In each case the conductivity was p-type.

The figure of merit Z is an indication of the efficiency of semiconductors as thermoelectric devices. It is computed by the following formula:

$$Z = \frac{Q^2}{\rho K}$$

where  K = thermal conductivity.

A value for K of $5 \times 10^{-3}$ cal/sec cm K° was assumed
since this is a value found for many thermosetting
materials (21).  For polymer 3A, $Z = 9.8 \times 10^{-10}$ (K°)$^{-1}$;
for polymer 19, $Z = 3.9 \times 10^{-10}$ (K°)$^{-1}$.  These values
are similar to those found by Engelhardt and Pohl (15)
and Opp (17).  The low figures of merit for the polymers
indicates that these materials have poorer thermoelectric
capabilities than the more conventional inorganic semi-
conductors.


C.   Electron Spin Resonance

            Estimates of the number of unpaired electrons
in samples of PAQR polymers at 25°C are listed in Table
6 together with the line width of the derivative curves
for the various electron paramagnetic resonance absorp-
tion spectra.  The line width in gauss is the distance
between points of zero slope on the derivative curves.
The PAQR polymers tested are characterized by a high
concentration of unpaired electrons.  There appears to
be a trend toward lower unpaired spin concentration as
the room temperature resistivity increases.  This was al-
so noted by Engelhardt and Pohl (15).

            A typical ESR spectrum is shown in Figure 5. The
sharp signal superimposed on the slightly broader signal

Table 6

Electron Spin Density in

PAQR Polymers

| Sample | Resistivity-25°C (ohm-cm) | Conc. of Unpaired Electrons (spins/g) | Line Width (gauss) |
|--------|---------------------------|---------------------------------------|--------------------|
| 3A | $2.0 \times 10^4$ | $2.4 \times 10^{19}$ | 3.5 |
| 19 | $2.4 \times 10^5$ | $4.0 \times 10^{19}$ | 3.4 |
| 7A | $6.5 \times 10^6$ | $1.3 \times 10^{19}$ | 7.7 |
| 26 | $9.5 \times 10^7$ | $1.7 \times 10^{19}$ | 5.0 |
| 6A | $1.1 \times 10^8$ | $1.8 \times 10^{19}$ | 6.7 |
| 21 | $6.0 \times 10^{11}$ | $9.6 \times 10^{18}$ | 8.3 |

## Table 7

### Electronic Parameters for Various
### PAQR Polymers Based on the Intrinsic Model

| Polymer | Resistivity 25°C ohm-cm | $\Delta E$ | Number Carriers/$cm^3$ | $10^5$ x $cm^2$/volt sec. Mobilities | |
| --- | --- | --- | --- | --- | --- |
| | | | | Holes | Electrons |
| 3A | $2.0 \times 10^4$ | 0.382 | $1.1 \times 10^{18}$ | 9.0 | 6.7 |
| 19 | $2.4 \times 10^5$ | 0.444 | $3.5 \times 10^{17}$ | 4.5 | 2.8 |
| 7A | $6.5 \times 10^6$ | 0.544 | $4.0 \times 10^{16}$ | -- | -- |
| 26 | $9.5 \times 10^7$ | 0.698 | $1.9 \times 10^{15}$ | -- | -- |
| 6A | $1.1 \times 10^8$ | 0.638 | $5.1 \times 10^{15}$ | -- | -- |
| 21 | $6.0 \times 10^{11}$ | 0.956 | $1.1 \times 10^{13}$ | -- | -- |

of the polymer is the lithium absorption. For estimat_
ing spin densities the polymer line was assumed to be
symmetrical.

Spectra could not be obtained for the polyben-
zimidazoles since they apparently have low spin densi-
ties. The spectrometer used was not able to detect a
significant signal (instrument sensitive to about $10^{15}$
spins/g).

D.    Band Theory, Carrier Concentration, and Carrier
      Mobilities

The number of carriers predicted by the simple
band theory for intrinsic semiconductors has been com-
puted for several PAQR polymers (see Table 7) (4,15).
The theoretical development of band theory is discussed
by Cusack (22). The carrier populations predicted by
band theory are much lower than the number of unpaired
electrons detected by ESR spectroscopy for most values of $\Delta E$.

It must be noted that organic materials do not
meet all the criteria for the rigid application of simple
band theory in interpreting their electronic behavior.
Nevertheless, the assumption of the intrinsic model is
useful for obtaining trends in carrier parameters.

The relationships between thermoelectric power
and carrier mobility, derived by Johnson and Lark-Horowitz

(23) were used to compute the mobilities reported in
Table 7. These relationships are reviewed by Engel-
hardt and Pohl (3,4,15). The values reported for car-
rier mobility are very low compared with conventional
organic semiconductors.

Engelhardt and Pohl (15) observed that the
band theory for an impurity type conductivity can not
be applied to these materials.

E.    Infrared Spectra and the Optical Absorption Threshold

The infrared spectra for several PAQR polymers
are shown in Figures 6-14. The spectra in general are
dissimilar except for those of samples 9A, 6A, and 5.
These three spectra are alike in almost every detail,
indicating that the chemical structures of the three poly-
mers are similar, This is not surprising, however, con-
sidering the reactants used to form these polymers. Poly-
mer 9A was produced by the melt polycondensation of phenol-
phthalein; polymer 6A was the condensation product of
phenol and phthalic anhydride (the reactants ordinarily
used to form phenolphthalein); and polymer 5 was produced
from phenolphthalein and phthalic anhydride.

Another observation of considerable interest is
that the resistivities observed for the three polymers are
also similar. The specific resistivities in ohm-cm for the

polymers are: $4.7 \times 10^8$ for polymer 9A, $1.1 \times 10^8$ for polymer 6A, and $8.8 \times 10^7$ for polymer 5.

This evidence seems to lend considerable support to the following argument proposed by Bornmann and Pohl (16): The resistivity of a PAQR polymer is a function of its molecular structure, and polymers of like structure should have the same resistivities. The converse, however, is not necessarily true. Polymers having similar resistivities may or may not have the same structure.

Bornmann and Pohl were not able to test their hypothesis sufficiently because they were unable to obtain good-quality infrared spectra.

Since the phenolphthalein polymers were among the first of the semiconducting polymers synthesized by workers in this laboratory (24), it is of particular importance to resolve the chemical structure of these materials. Therefore, the problem will be given special attention in a later section of this paper.

The presence of an aromatic type structure in the polymers examined is evidenced by the presence of bands for $=$C-H stretching vibrations near 3000 cm$^{-1}$ and bands for $-$C $=$ C$-$ vibrations in the 1600-1500 cm$^{-1}$ region. Also, aromatic absorption bands associated with out-of-plane C-H bending vibrations are prominent between 950 and 650 cm$^{-1}$ (25).

The black color of the PAQR polymers indicates that they absorb indiscriminantly through the visible region into the infrared. Ultraviolet and visible absorption spectra confirm this. It can be seen that their transparency occurs around the beginning of the medium infrared range at wavelengths corresponding to the observed thermal energy gap. This phenomenon has been observed by other workers (20,26,27) in the past. Kmetko (26) and Andrew (27), working with a series of charred cellophane films showed that the energy gap calculated from the wave length at which the optical absorption was equal to half its minimum value was about equal to that deduced from the slope of the resistivity temperature curve. The exact location of this optical threshold is somewhat ambiguous, however, and has been found to be highly dependent on the thickness, or in this case concentration, of the sample (28).

Figures 13 and 14 show absorption spectra of polymer 3A and illustrate the effect of increasing the concentration of polymer in a KBr pellet. For the higher concentration of polymer the intensity of absorption, of course, increases; but there is also better resolution in the region above 10 microns.

## Discussion

From the preceeding discussion and the obser-
vations of other workers it is apparent that semicon-
ducting organic polymers are characterized by: (a) a
high degree of conjugation; (b) a negative temperature
coefficient of resistivity; (c) a high concentration
of unpaired electrons at ordinary temperatures; and (d)
a large number of relatively immobile carriers compared
with conventional inorganic semiconductors). Increasing
the length of the conjugated chain in linear and cross-
linked polymers brings about a sharp increase in the
concentration of unpaired delocalized π-electrons which
gives the materials high thermal stability and relative
inertness to addition reactions (1).

Berlin (1,10) attributes the observed paramag-
netism of polymers having enhanced electrical properties
to the presence of stable biradicals at ordinary temper-
atures, and cites considerable chemical evidence which
lends credence to this view. He has observed that in the
polymerization of linear polyalkynes and polyphenylenes
only materials of relatively low molecular weight are
formed. This, according to Berlin, may be explained in
the following way: The growth of a conjugated polymer
chain is accompanied by an increase in the radical sta-
bility (biradical), which results from the increased

degree of delocalization of electrons in the chain.
Within a limit, a radical is formed which is not able
to grow under the conditions of reaction. Such in-
active biradicals are formed with particular ease in
the presence of a continous system of conjugated bonds
between unpaired electrons. This behavior is very dif-
ferent from that observed in the polymerization of vinyl
monomers.

The evidence, therefore, indicates that even
at room temperature and lower, high molecular weight con-
jugated macromolecules exist in the form of stable bira-
dicals; that the greater the molecular weight of a con-
jugated polymer, the greater the concentration of biradi-
cals present should be; and that the enhanced electronic
behavior of these materials is directly related to the
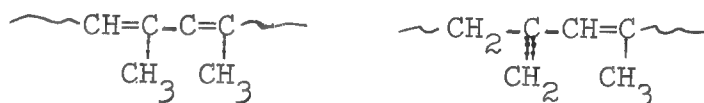biradical population which may be observed by electron
spin resonance spectroscopy.

There is also substantial physical evidence
which supports this view. Figure 15 is a summary of data
obtained in this investigation and data obtained by sev-
eral other workers (11,15,17), plotted on logarithmic
coordinates, which appear to indicate a definite trend to-
ward enhanced conductivity in polymers having a high con-
centration of unpaired electrons. Pohl and Engelhardt
(4,15,28) have proposed an explanation for this observed

behavior by assuming the existance of stable biradi-
cals. Their explanation seems to offer at least a
qualitative description of the experimental facts.

If all this is true, however, how does one
account for the relatively poor electronic properties,
light colors, and lack of paramagnetic response of the
polybenzimidazoles which are supposedly completely con-
jugated polymers containing heteroatoms in the chain of
conjugation? Once again, an argument proposed by Berlin
(1) to explain the relatively poor electronic properties
he observed in polyarylacetylenes seems to apply in this
case as well. Berlin and his associates found that the
polyvinylenes they synthesized were polydisperse, having
a small high molecular weight fraction composed of poly-
mer molecules with uninterrupted conjugation and a degree
of polymerization much greater than the average degree
of polymerization of the unfractionated polymer. Electro-
physical characterization of these fractions showed that
the long chain molecules possessed sufficient conjugation
to exist as stable biradicals even at room temperature.
But the major portion of each polymer was low molecular
weight material with molecules not having the degree of
conjugation necessary to exist as biradicals at room tem-
perature. Since the major portion of these polymers did
not contain unpaired electrons, the materials, did not

exhibit enhanced electronic properties.

This polydispersity should also account for the relatively poor conductivities observed for the polypropyne and polyphenylacetylene samples tested here. In addition, it is possible that in polypropyne the continuity of the conjugated chains may be broken by a redistribution of the C=C bonds in the molecule (1).

$$\sim CH=\underset{\underset{CH_3}{|}}{C}-\underset{\underset{CH_3}{|}}{C}=\underset{}{C}\sim \qquad \sim CH_2-\underset{\underset{CH_2}{\|}}{C}-CH=\underset{\underset{CH_3}{|}}{C}\sim$$

The low values for the thermal energy intervals of the polyalkynes are difficult to explain. The single value of resistivity for polypentyne-1 should not be considered reliable and therefore does not warrant discussion. Suffice it to say, however, that additional work is necessary to characterize the polyalkynes and determine precisely what factors affect the electrical properties of these polymers.

Another Soviet scientist, N.N. Semenov (9), apparently disregards the notion of polydispersity proposed by Berlin. By considering monomeric conjugated systems and conjugated polymers together and assuming all the molecules to be identical, he notes that the number of unpaired electrons per molecule is always found to be fractional. Because of this, Semenov contends that it is not proper to speak of any individual unpaired electron,

but only of the extent of unpairing of the electron cloud as a whole. Unpairing, therefore, is apparently associated with the ground state of the molecule, not with the excited state.

In further considering the observed paramagnetic properties of conjugated polymers, Semenov notes that ESR lines associated with polymeric materials are either broad or narrow and sharp. The narrow ESR lines, he claims, give evidence of the existence of individual collective levels in which electrons occur in a delocalized form throughout a conjugated system (molecule). Those materials with broad ESR lines have regions with strongly interacting electron clouds of individual collective levels or domains. Therefore, it follows that the conductivity of a polymeric material is determined by the state of the sample as a whole, rather than simply by the structure of the individual molecules. In conjugated systems of both types (showing narrow or broad ESR signals), generalized levels exist, and apparently there is practically no resistance to the motion of electrons under the influence of an external magnetic field in the conjugated molecule itself, or in the domains as well. Resistance appears only when the electron passes from one polymer molecule to another. Since a domain is considerably larger in volume than a

polymer molecule, systems having domains should be expected to show considerably larger values of electrical conductivity.

In surveying the work of other Soviet scientists Semenov finds that enhanced conductivity is, in general, observed in the same polymers that have broad ESR signals. On the other hand, many polymers with continuous conjugated chains having narrow ESR lines do not exhibit enhanced electrical conductivity at room temperature and usually have high thermal energy intervals.

He also noted that there is a distinct relation between the change in the thermal energy interval and the pre-exponential factor $\rho_0$ for different materials. Figure 16 is a plot of data obtained in this investigation and by others in this Laboratory (15, 17). It can be seen that there is a good linear relationship between $\log \rho_0$ and $\Delta E$ for those polymers that exhibit relatively poor semiconducting properties. The materials showing a sharp deviation from linearity have lower resistivities and thermal energy intervals.

Semenov suggests that sharp deviations from linearity on the $\Delta E$ vs. $\rho_0$ plot should represent systems with strong collective interactions and broad ESR lines, while those substances which obey the linear relation should be expected to have narrow, sharp ESR lines.

He does not, however, show sufficient ESR data to support his argument.

Figure 16 shows that PAQR polymers do not obey the linear relationship, but they do exhibit sharp ESR signals. Hatano, Kambara, and Okamoto (11) observed high conductivities and low thermal energy intervals in highly crystalline stereoregular polyacetylenes where one might expect to find a high degree of collective interactions. In fact, these materials did have considerably higher conductivities than amorphous polyacetylenes. In all cases, however, sharp narrow ESR lines were found.

The difficulty in detecting any apparent ESR signal for the polybenzimidazoles where Semenov would predict a sharp signal is also puzzling, since the polybenzimidazoles do seem to obey the linear relationship.

These observations are in direct contradiction to the hypothesis forwarded by Semenov and appear to add additional support to the views of Berlin. The physical state of a material, however, does seem to be important in determining its electronic properties.

In discussing the PAQR polymers it should be clear that they are complex, apparently highly crosslinked (they are insoluble and infusible but the extent of crosslinking has not been determined), deeply colored,

aromatic materials whose structure is still very much in doubt. Bornmann and Pohl (16) made serious attempts to confirm spectroscopically the structure of the phenolphthalein PAQR polymers but were unsuccessful because they were not able to obtain good quality spectra by the mull technique.

In the pressed pellet technique, however, a smaller particle size is possible and there is better distribution of particles in the suspending medium. This results in a great decrease in scattering losses and a sharpening of the absorption bands. Moreover, there are no obscuring bands such as occur with mulling agents, and samples once prepared can be conveniently stored for future reference.

With the aid of infrared spectra obtained by the KBr pellet technique it is now possible to propose a structure for the phenolphthalein PAQR polymers.

Jakobsen and Wyant (3) examined the infrared spectra of ten 3,3-bis(phenyl) phthalides (II) together with those of phthalide (I) and phthalic anhydride in the region of 2000 to 330 $cm^{-1}$ to determine what frequencies were characteristic of the phthalide ring and effects of phenyl substitution in the 3-position of the phthalide ring system.
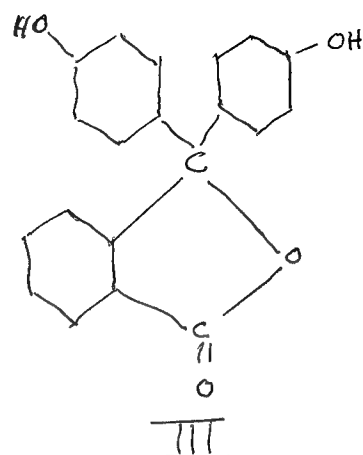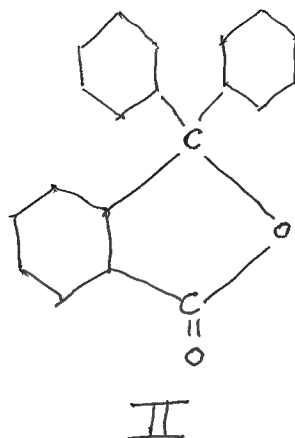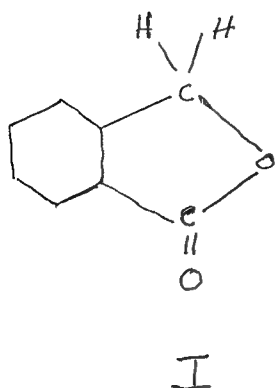
They observed bands characteristic of the phthalide ring at 1279-1289 cm$^{-1}$, 1100-1117 cm$^{-1}$, 1011-1020 cm$^{-1}$, 490-516 cm$^{-1}$, 470-488 cm$^{-1}$. Bands characteristic of the 3,3-bis (phenyl) phthalides (11), but not found for phthalide itself, were observed at 626-637 cm$^{-1}$, 521-539 cm$^{-1}$, and 355-384 cm$^{-1}$, All the compounds studied showed a lactone carbonyl absorption between 1710 cm$^{-1}$ and 1776 cm$^{-1}$. They also noted that for phenyl rings with hydroxyl substituion (III) a band was always found at 607-616 cm$^{-1}$.

This investigation thus served to demonstrate the importance of the far infrared region (the cesium bromide region above 650 cm$^{-1}$) in spectroscopic investigations of molecular structure. The far infrared region can be a valuable aid to the type of structural confirmation being sought here.

The infrared spectrum of sample 9A (Figure 6) shows a strong carbonyl absorption at 1760 cm$^{-1}$ and bands at 1275, 1097, and 1008 cm$^{-1}$, all of which are characteristic phthalide absorption frequencies. Moreover, the bands at 628 and 607 cm$^{-1}$ are characteristic of 3,3-bis (phenyl) phthalides and hydroxyl substituted 3,3-bis(phenyl) phthalides, respectively. Therefore it may be argued that the basic structural unit of the polymer is the phenolphthalein (III) repeating unit. Additional evidence of this should be sought by examining the spectral region from 600-330 cm$^{-1}$ to see whether the other 3,3-bis(phenyl) phthalide absorption bands are present.

The rules of aromatic substitution indicate that substitution on phenolphthalein should occur in positions ortho to the phenyl hydroxyl groups. Moreover, an examination of a molecular model of phenolphthalein indicates that the positions on the phenyl rings meta to the hydroxyl groups are quite inaccessible (i.e.) sterically blocked) to attack in addition to being electronically deactivated.

With this in mind, the next step is to examine the region above 950 cm$^{-1}$ to see if it is possible to determine the position of the substituents on the phenyl groups from the in-phase-bending vibrations of the remaining C-H bonds. In Figures 6-8 bands in this region are located at 948, 881, 819, 754, and 689 cm$^{-1}$.

Randle and Whiffen (31) have prepared tables of characteristic vibration frequencies for all types of substituted benzenes. These frequencies, they note, are essentially independent of the type substituent but depend only on the number of consecutive hydrogens remaining on the substituted aromatic ring.

Careful comparison of the absorption patterns for the three phenolphthalein polymers with the data presented by Randle and Whiffen indicates that their patterns closely resemble only that for substitution where one isolated aromatic hydrogen and two consecutive aromatic hydrogens are both present. For this type of substitution the tables indicate bands at $929 \pm 11$, $868 \pm 11$, $816 \pm 14$, $744 \pm 7$ and $706 \pm 6$ cm$^{-1}$. This evidence strongly supports the view that substitution is _ortho_ to the hydroxyl groups on the phenyl rings. One might also expect to find the absorption pattern for 4 adjacent hydrogens if the aromatic ring of the phthalide group is substituted. But these bands occur at frequencies of $934 \pm 11$, $865 \pm 14$, and $751 \pm 7$ cm$^{-1}$ which effectively overlap those mentioned above.

With this strong spectroscopic evidence, it is possible to predict two types of substituted phenolphthalein groups which cannot be readily differentiated with infrared spectroscopy by virtue of similar numbers of adjacent free hydrogen atoms on their 3,3-phenyl rings.
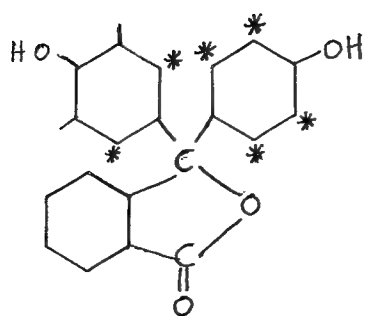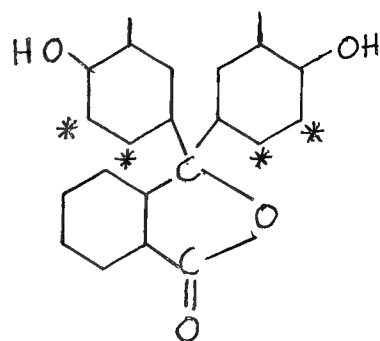
(A)                                    (B)

The enhanced electronic conduction and strong ESR signals observed for these materials certainly suggest that they have highly conjugated structures. Therefore, choosing between the two possibilities may not be as difficult as it seems if it is noted that structure (A) is a conjugated structure and structure (B) is not. If structure (A) predominates, a network of the following type is probably formed:
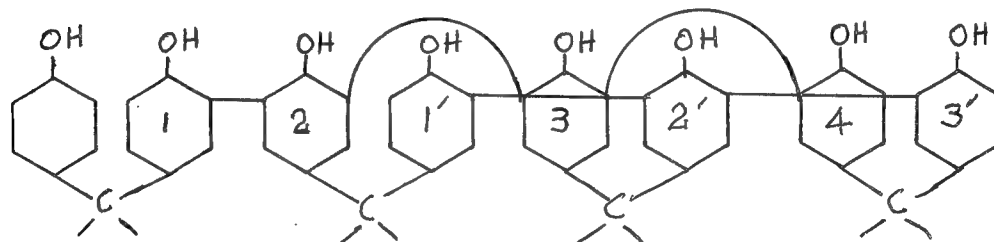


where continuous conjugated chains of hydroxyl substituted phenyl groups are present.
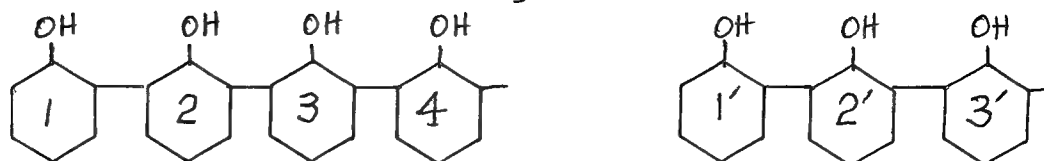
This picture is undoubtedly an oversimplification since such a structure would actually be a 3-dimensional crosslinked network. The extent of crosslinking in these polymers is not known, and additional chemical and kinetic studies need to be carried out to determine this.

It is also likely that type (B) substitution would be present to some extent in any polymer formed. This structure would serve to decrease the degree of conjugation in the polymer and may account for the resistivities of the phenolphthalein polymers being as high as $10^8$ ohm-cm.

Additional chemical studies are necessary to confirm the proposed structure for the phenol phthalein polymers. One study which might prove whether or not the aromatic ring of the phthalide group participates in the crosslinking reaction is to attempt polymerization with a tetra-substituted phthalide aromatic ring (IV).
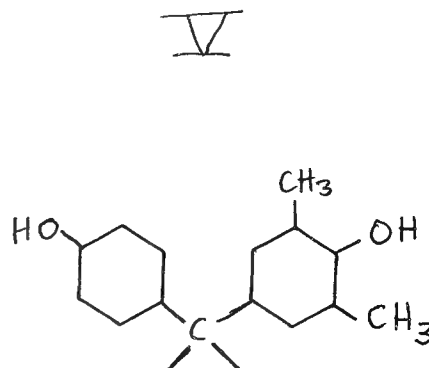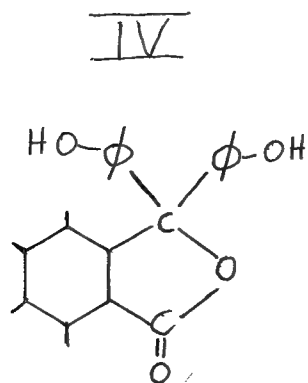
If a crosslinked polymer were formed, this would be a good indication that substitution occurs on the 3-phenyl rings. Another study which would tend to prove the proposed structure is the polymerization of a phenolphthalein with one of its 3-phenyl rings disubstituted in the positions ortho to the aromatic hydroxyl (V). In this case a linear polymer with perhaps even more greatly enhanced electronic properties might be formed. The molecular weight of such a polymer could then be studied by useful techniques such as light scattering.

Since all of the evidence is consistent with the presence of a poly-phenolphthalein structure, this will serve as a useful working hypothesis in the future for relating the electrical properties to the structure of these polymers.

## Conclusions

1. The PAQR polymers studied here have electrical and
   magnetic properties typical of this class of polymers
   with resistivities ranging from $10^4$ to $10^{11}$ ohm-cm;
   thermal energy intervals ranging from 0.35 to 0.8 eV;
   sharp electron spin resonance absorption spectra and
   high concentrations of unpaired electrons; low carrier
   mobilities; positive Seebeck coefficients indicating
   p-type conductivity; and low figures of merit.

2. Polybenzimidazoles appear to have relatively poor
   electrical properties with resistivities of $10^{10}$ to
   $10^{16}$ ohm-cm: thermal energy intervals of 1 to 3 eV;
   and no detectible electron spin resonance absorption.
   These poor properties are probably due to a large low
   molecular weight tail on the molecular weight distri-
   bution and the resultant low concentration of stable
   biradicals present in the polymers at ordinary temper-
   atures.

3. The polyalkynes studied have high resistivities (about
   $10^{10}$ ohm-cm) but relatively low thermal energy intervals
   (about 0.5 to 0.7 eV). These properties are quite puz-
   zling; additional study of this class of polymers is
   necessary to obtain a better understanding of how their
   electrical properties are related to chemical structure.

4. There is a definite relationship between spin density and conductivity in conjugated polymers. This indicates that the unpaired electron concentration in these materials is directly related to the number of free carriers and that carrier mobilities may be relatively unimportant in determining the conductivity.

5. There is a distinct relation between the change in thermal energy interval and in the coefficient $\rho_0$ for polymeric materials with high resistivities and high $\triangle E$ values. This is a linear relationship when $\triangle E$ is plotted versus log $\rho_0$. Polymers with low resistivities and low $\triangle E$ values do not follow this linear relationship.

6. Infrared absorption spectra have been obtained for several PAQR polymers and a conjugated structure based on a phenolphthalein repeating unit has been proposed for the phenolphthalein PAQR polymers. This structure is consistent with available chemical and spectroscopic evidence.

7. The infrared spectra obtained provide definite evidence that polymers with similar structures should be expected to have the same resistivities.

8. The KBr pressed disk technique has been established as a technique of general applicability in obtaining infrared spectra for deeply colored insoluble and infusible macromolecular materials.

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    were provided by the Polymer Corporation Limited,
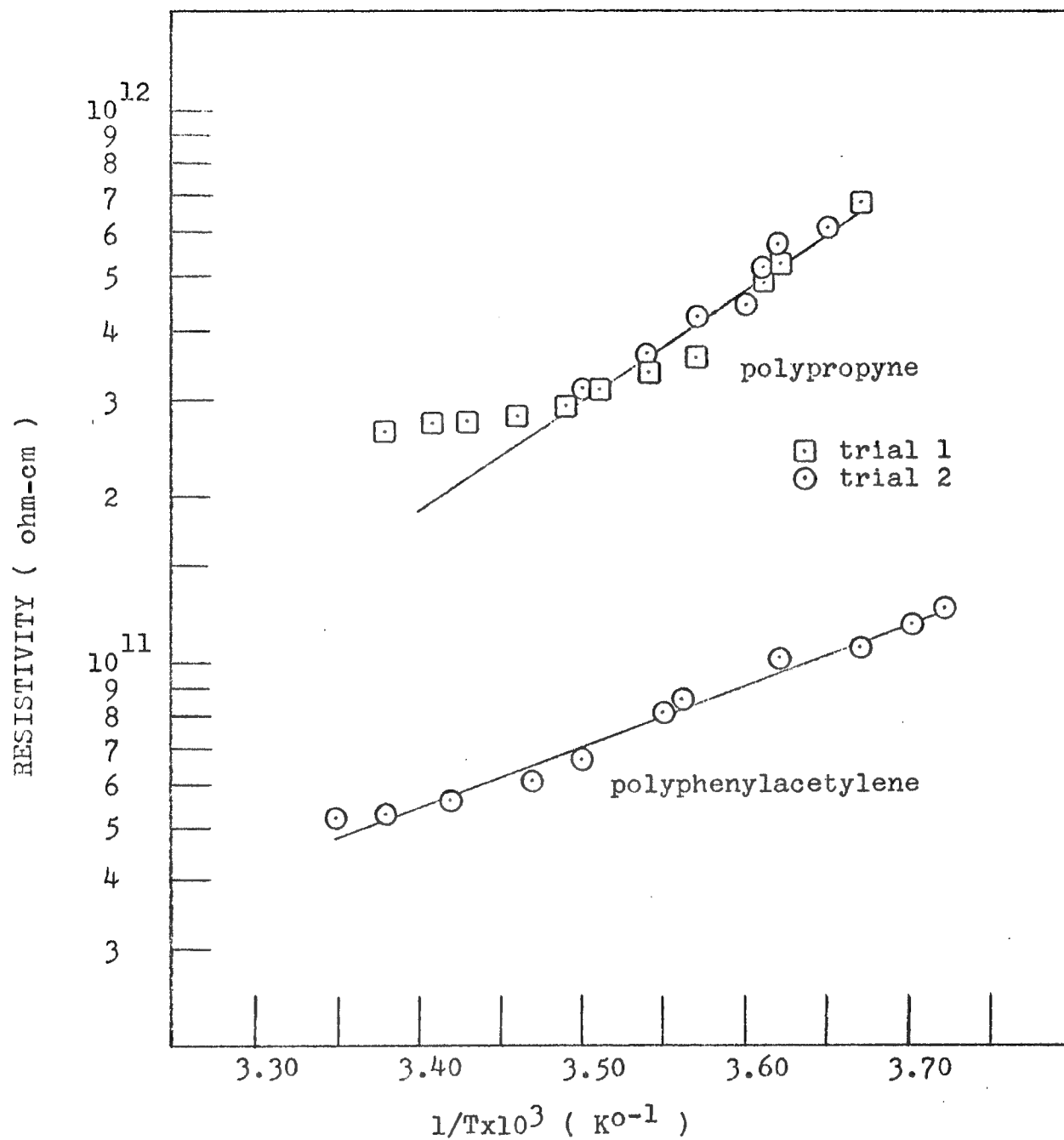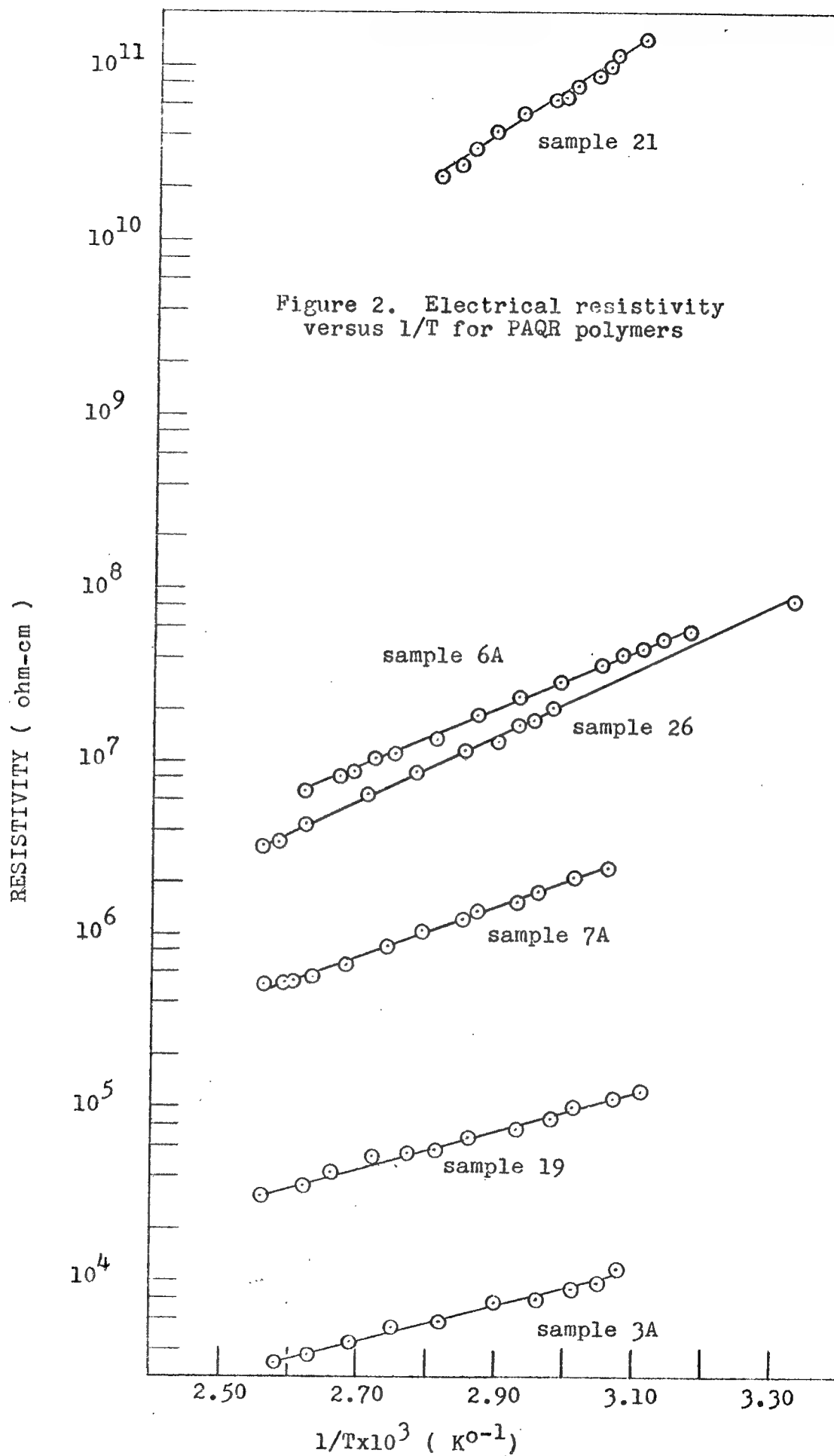    Sarnia, Ontario.

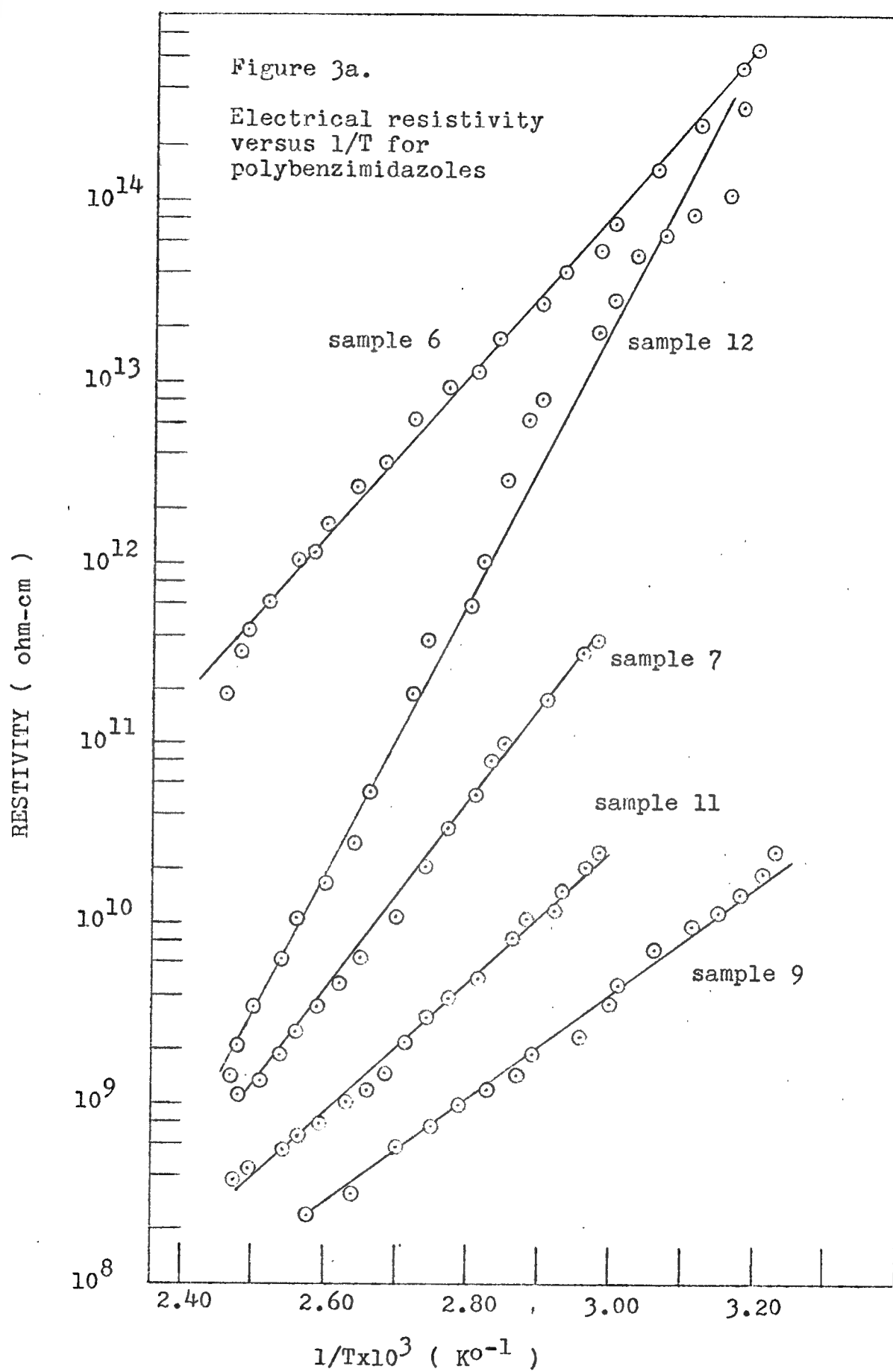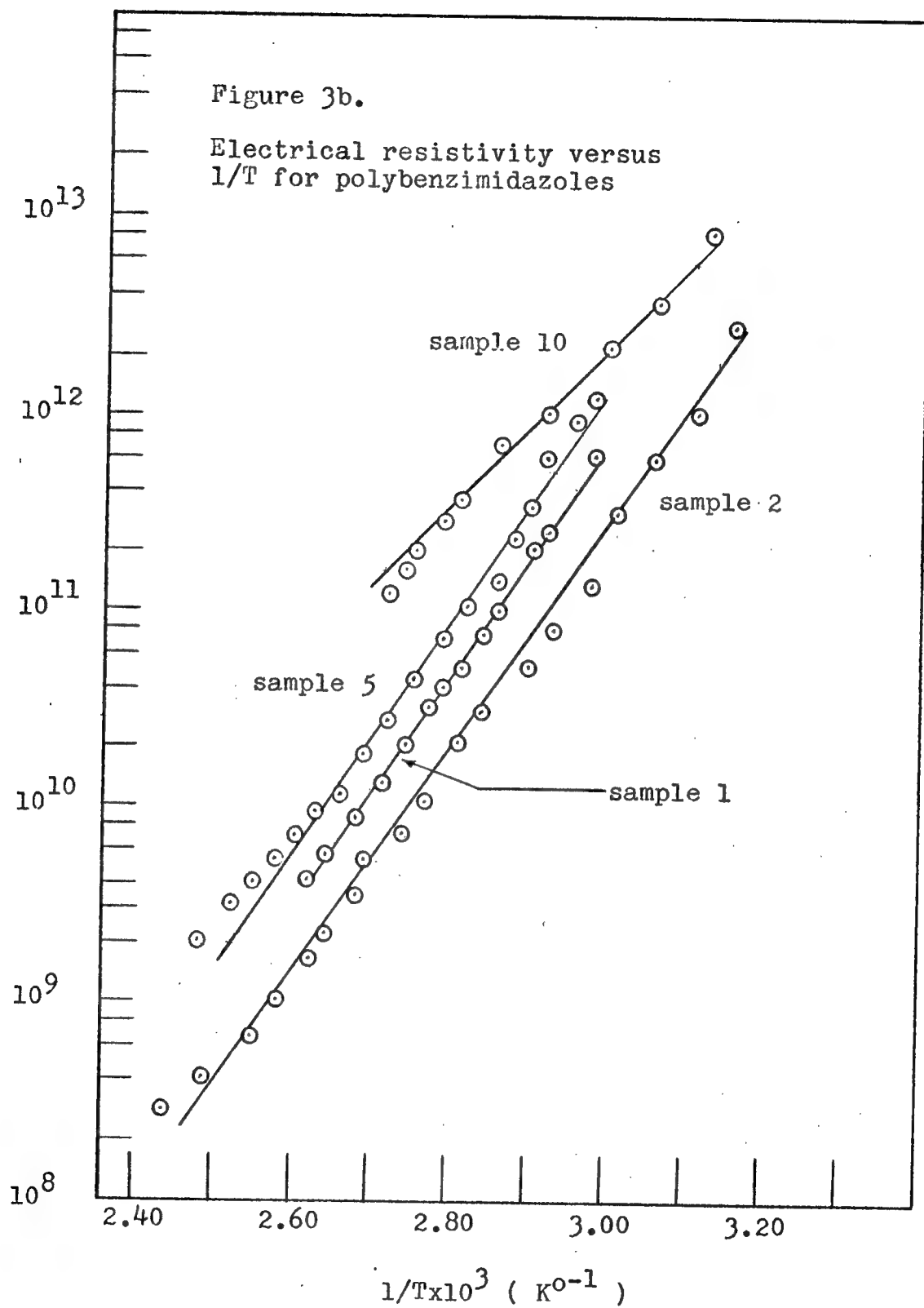Figure 1. Electrical resistivity versus 1/T for polyalkynes

Figure 2. Electrical resistivity versus 1/T for PAQR polymers

Figure 3a.

Electrical resistivity versus 1/T for polybenzimidazoles

Figure 3b.

Electrical resistivity versus
1/T for polybenzimidazoles

sample 10

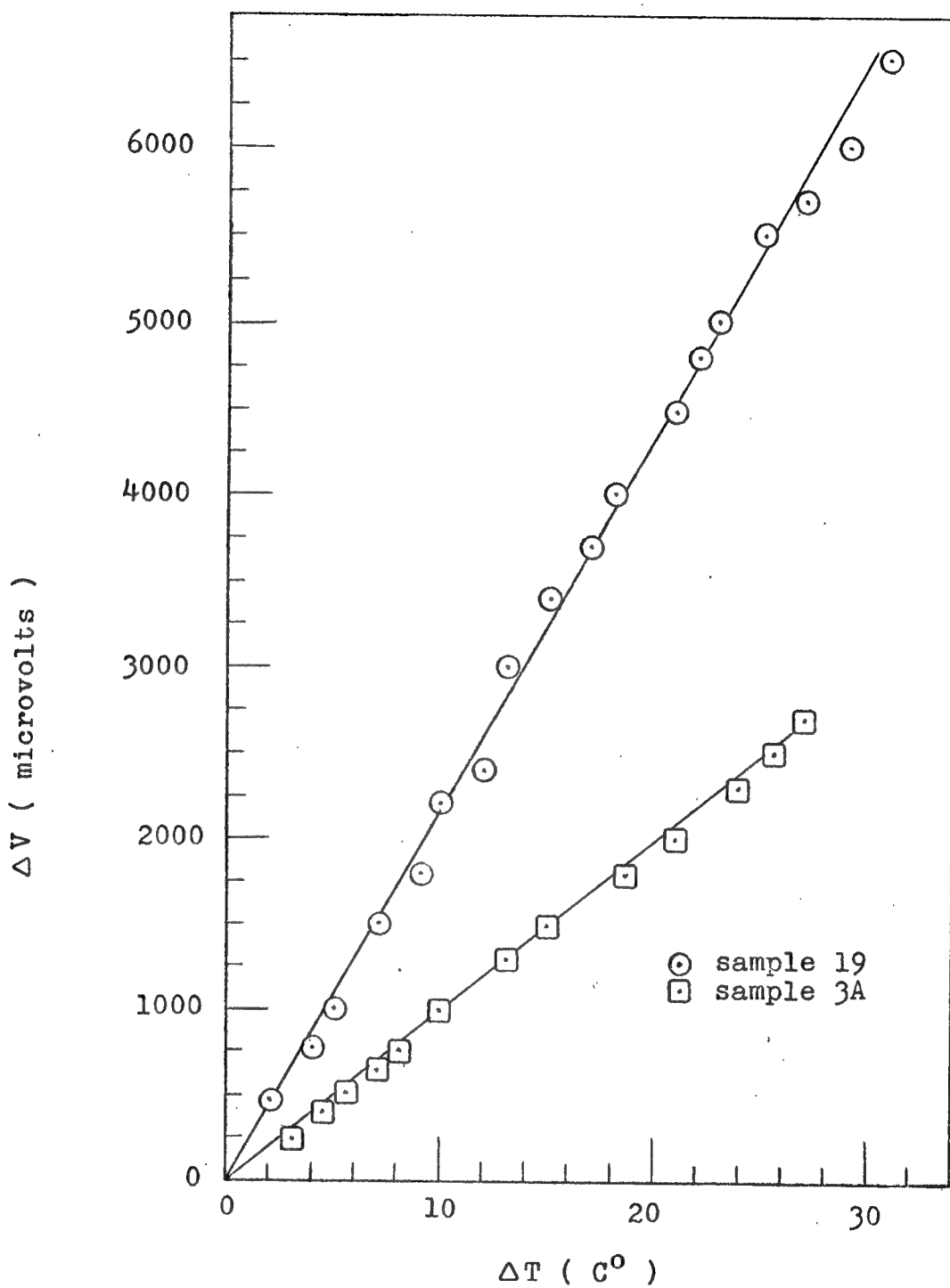sample 2

sample 5

sample 1

$1/\text{Tx}10^3$ ( $K^{o-1}$ )

Figure 4.   Variation in induced emf with
thermal gradient for PAQR
polymers
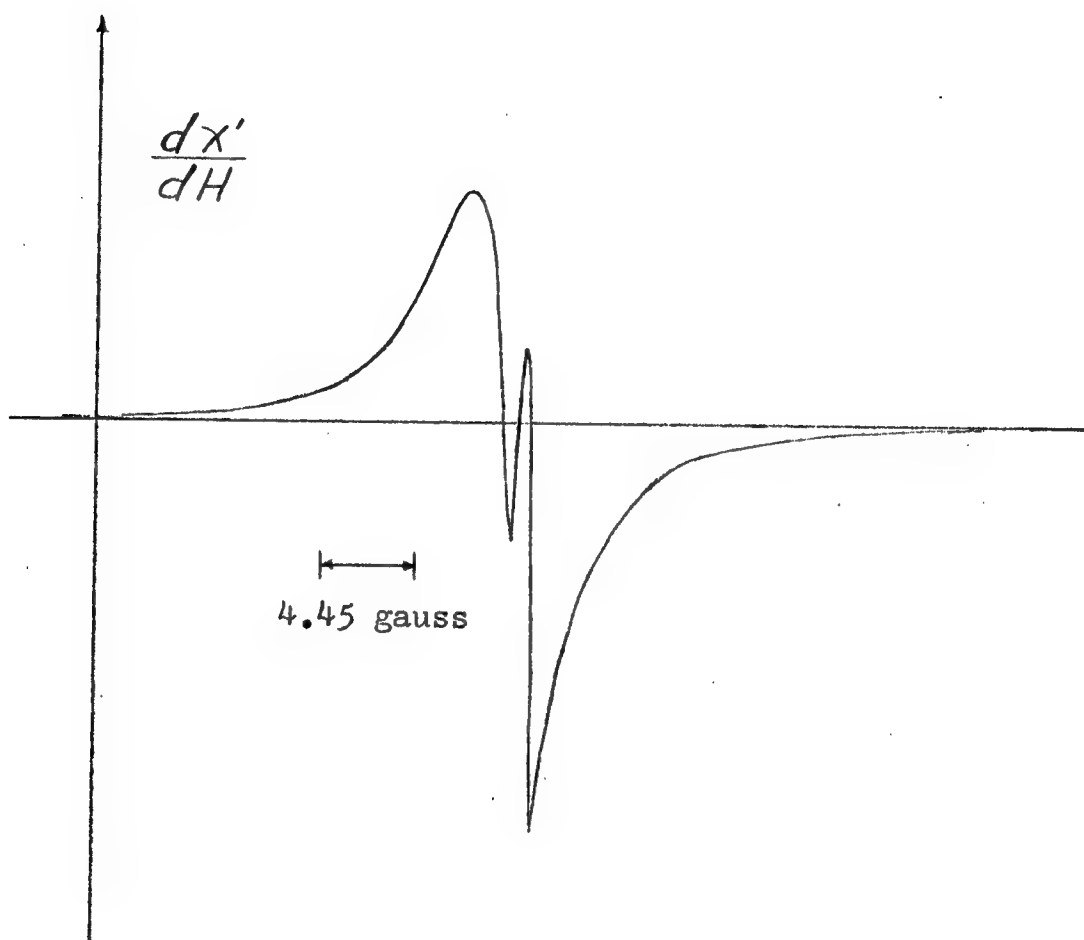
Figure 5.   Electron spin resonance
spectrogram for Sample 19

Figure 6
I.R. spectrum
of sample 9A

Figure 7
I.R. spectrum
of sample 5

Figure 8
I.R. spectrum
of sample 6A

Figure 9
I.R. spectrum
of sample 19

Figure 10
I.R. spectrum
of sample 26

Figure 11

I.R. spectrum

of sample 13



Figure 12

I.R. spectrum

of sample 22

Figure 18
I.R. spectrum
of sample 3A
(high concentration)

Figure 19
I.R. spectrum
of sample 3A
(low concentration)

Figure 15.

Relation between unpaired electron concentration and resistivity for data presented by several workers

Figure 16. Relation between $\Delta E$ and $\rho_0$ for polymers studied by several workers

Legend:
□ ref. 15
⊙ ref. 17
▲ this study—
▲ PAQR
⊙ polybenzimidazole
◁ polyalkyne

LOG $\rho_0$

$\Delta E$

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